

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 074-0188

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE March 1997	3. REPORT TYPE AND DATES COVERED Technical	
4. TITLE AND SUBTITLE Separation of RDX from Composition B Via a Supercritical Fluid Extraction Process			5. FUNDING NUMBERS N/A	
6. AUTHOR(S) Jeffrey B. Morris				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory AMSRL-WM-PC Aberdeen Proving Ground, MD 21005-5066			8. PERFORMING ORGANIZATION REPORT NUMBER N/A	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) SERDP 901 North Stuart St. Suite 303 Arlington, VA 22203			10. SPONSORING / MONITORING AGENCY REPORT NUMBER N/A	
11. SUPPLEMENTARY NOTES Published in Proceedings of 1997 JANNAP Safety & Environment Protection Subcommittee Meeting, CPIA Pub. 647, Vol. I., Marcy 1997, pp. 283-290The United States Government has a royalty-free license throughout the world in all copyrightable material contained herein. All other rights are reserved by the copyright owner.				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release: distribution is unlimited.				12b. DISTRIBUTION CODE A
13. ABSTRACT (Maximum 200 Words) Supercritical fluid extraction is used, on the laboratory scale, to successfully separate and recover RDX from Composition B high explosive using neat carbon dioxide as the extraction solvent. The nitramine is recovered from Composition B with a purity in excess of 99%. TNT is readily extracted from Composition B, along with most of the wax, leaving the majority of RDX as an unextracted crystalline solid in the extraction vessel. Processing conditions for this separation process are discussed, including, including temperature, pressure, and solvent-to-feed ratio.				
14. SUBJECT TERMS RDX supercritical fluid Composition B TNT SERDP SERDP Collection				15. NUMBER OF PAGES 9
				16. PRICE CODE N/A
17. SECURITY CLASSIFICATION OF REPORT unclass.		18. SECURITY CLASSIFICATION OF THIS PAGE unclass.	19. SECURITY CLASSIFICATION OF ABSTRACT unclass.	
			20. LIMITATION OF ABSTRACT UL	

**SEPARATION OF RDX FROM COMPOSITION B VIA A SUPERCRITICAL FLUID
EXTRACTION PROCESS**

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Paper presented at 1997 JANNAF Joint Propellant Development & Characterization Subcommittee and Safety & Environmental Protection Subcommittee Meeting, NASA Ames Research Center, CA, March 1997. Published in Proceedings of 1997 JANNAF Safety & Environmental Protection Subcommittee Meeting, CPIA Pub. 647, vol.I., March 1997, pp. 283-290.

19990525 016

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ABSTRACT

Supercritical fluid extraction is used, on the laboratory scale, to successfully separate and recover RDX from Composition B high explosive using neat carbon dioxide as the extraction solvent. The nitramine is recovered from Composition B with a purity in excess of 99%. TNT is readily extracted from Composition B, along with most of the wax, leaving the majority of RDX as an unextracted crystalline solid in the extraction vessel. Processing conditions for this separation process are discussed, including temperature, pressure, and solvent-to-feed ratio.

INTRODUCTION

Conventional demilitarization techniques - such as open burning or open detonation - designed to dispose of excess ordnance items that contain energetic materials are being phased out due to concerns regarding their impact on the environment. These disposal techniques are often wasteful, resulting in the destruction of potentially valuable energetic materials. Alternate technologies need to be developed for the demilitarization of these ordnance items in an environmentally-friendly manner. Resource recovery of the energetic materials in these items should be an important consideration in the development of new demilitarization technologies.

Ordnance items containing high explosive fills consisting of 2,4,6-trinitrotoluene (TNT) and nitramines such as cyclotrimethylenetrinitramine (RDX) or cyclotetramethylenetetranitramine (HMX) represent a significant portion of the U.S. conventional ammunition demilitarization stockpile. One example of a such a fill is Composition B high explosive, which consists of RDX and TNT, nominally in a 60:40 weight ratio, with about 1% added desensitizing wax. The military grade RDX that is used in Composition B also contains a small amount of HMX impurity, typically in the range of 5% by weight. Composition B, and other TNT-based explosives, are removed in practice from artillery shells via melt-out or steam-out operations. Recovered Composition B from a melt-out/steam-out operation is expected to be far from ideal for reuse as a Composition B fill. However, this material is a suitable candidate for recovery of RDX for reutilization if an appropriate chemical processing technology is developed.

One technology under investigation for the recovery of RDX from Composition B is supercritical fluid extraction (SFE). Carbon dioxide is widely used in SFE processes, is generally accepted as an environmentally-friendly processing solvent for "green" technologies, and is fairly inexpensive. Quantitative solubility data for RDX, measured at the U.S. Army Research Laboratory (ARL), was presented in a previous JANNAF paper.[1] RDX is found to display a limited solubility in neat carbon dioxide over a range of pressures up to 7,000 lb/in² and temperatures up to 80 °C. The maximum solubility of RDX observed within this temperature range is approximately 0.25 mg RDX per gram of carbon dioxide. Quantitative solubility data for TNT, measured at the Fraunhofer Institut für Chemische Technologie (ICT), was presented in a paper at a recent International Annual Conference of ICT.[2] The workers at ICT measured TNT solubilities as high as 55 mg TNT per gram of carbon dioxide (5.2 wt % TNT). The solubilities of TNT relative to RDX are determined using the data found in references 1 and 2, and are presented in Table 1; the TNT solubility data from reference 2 is interpolated to the pressure and temperature conditions reported in this table. As can be seen in Table 1, TNT has a solubility in neat carbon dioxide that is 2 - 3 orders of magnitude greater than that of RDX. It should be possible to exploit the large difference in the solubilities of these two energetic materials to selectively extract TNT in the presence of RDX.

Table 1. Solubility ratios of TNT^a relative to RDX^b in carbon dioxide as a function of temperature and pressure.

	30 °C	35 °C	50 °C	65 °C	80 °C
2,000 lb/in ²		740			
4,000 lb/in ²	560	540	380	260	170
6,000 lb/in ²	610	520	470	>320 ^c	>230 ^c
7,000 lb/in ²	720	790	>490 ^c	>320 ^c	>220 ^c

^a TNT solubility datum at 35 °C and 2,000 lb/in² is from reference 1; all other TNT solubility data used is interpolated from data in reference 2.

^b RDX solubility data from reference 1.

^c Estimated values; no TNT solubility data were measured at these temperatures and pressures.

EXPERIMENTAL

A block schematic of the experimental apparatus is shown in Figure 1. A syringe pump (ISCO model 260D) is filled with neat carbon dioxide. The pump can be used up to a maximum operating pressure of 7,500 lb/in². The syringe pump is equipped with a water jacket to stabilize the temperature of the pump. Initially, the water jacket is chilled to about 10 °C to increase the efficiency of filling the pump with liquid carbon dioxide. After the pump is filled with carbon dioxide, the set point of the water recirculator (not shown in Figure 1) for the water jacket is set to the temperature that the extraction will be carried out at, and the pump is brought up to pressure. The pump is allowed to stabilize in temperature and pressure for about an hour. The pump is equipped with digital pressure and syringe displacement readouts. The displacement readout is used to determine the volume of carbon dioxide used during the extraction. The density of the carbon dioxide within the pump is determined from its temperature and pressure using the ISCO computer program *SF Solver*.^[3] The mass of carbon dioxide used in an extraction is easily calculated from the carbon dioxide volume and density.

Extractions are carried out in a stainless steel 7.5-ml volume high pressure extraction vessel (Keystone Scientific) that is rated for a maximum operating pressure of 10,000 lb/in² at 150 °C. Single 1/4-inch diameter pieces of Composition B are sealed in the extraction vessel. The Composition B sample mass ranged from 150 mg to 800 mg. The vessel is installed into the extraction unit, is pressurized with carbon dioxide, and is brought up to temperature. After the thermal set point of the extraction unit has been reached, the carbon dioxide is allowed to flow from the syringe pump, through the extraction vessel (from bottom to top), and is expanded through a heated variable flow restrictor (ISCO). The TNT and wax that is extracted from the Composition B sample is observed to nucleate as the carbon dioxide is expanded from a liquid or dense gas - the density of carbon dioxide at 5,500 lb/in² and 80 °C is 0.81 g/ml - to a gas at ambient pressure and temperature.

High pressure liquid chromatography (HPLC) is used to determine the relative quantities of RDX, HMX, and TNT in the unextracted Composition B, the extracted TNT, and the nitramine left behind in the extraction vessel. Chromatographic conditions include the use a C18 column, a mobile phase consisting of 75% water and 25% methanol, a mobile phase flow rate of 1 ml per minute, and ultraviolet detection at 246 nm. Solutions are passed through a 0.45 µm filter prior to loading of the 10 µl sample injection loop.

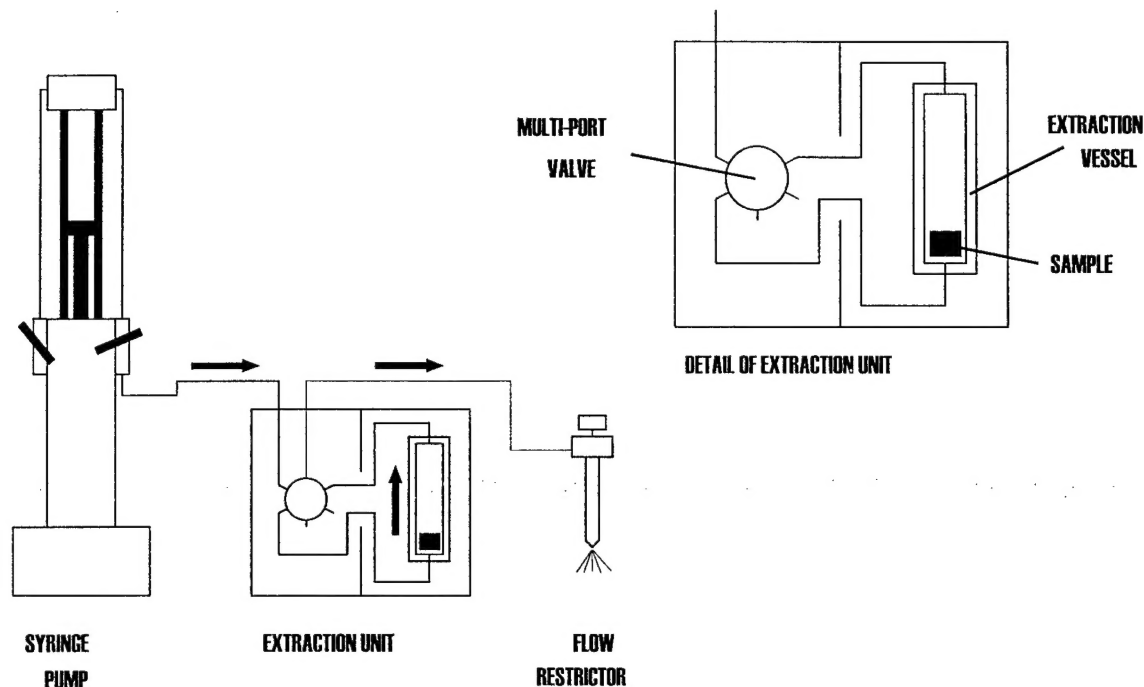


Figure 1. Block schematic of the supercritical fluid extraction apparatus.

RESULTS AND DISCUSSION

Extraction of Composition B using neat carbon dioxide. The ability to selectively remove TNT in the presence of RDX is initially demonstrated on a 50:50 (by weight) mixture of the two explosives. A 292 mg sample of the RDX/TNT mixture is placed in the 7.5-ml extraction vessel and the vessel is installed in the extraction unit. The extraction is carried out at 50 °C and 2,000 lb/in² using a large excess - 210 grams - of carbon dioxide. The material remaining behind in the extraction vessel is found to contain less than 1% TNT when analyzed via HPLC. Analysis of the extracted TNT reveals that about 2 mg of RDX is also extracted. The quantity of RDX extracted is consistent with the solubility values in reference 1 for the amount of carbon dioxide used.

Supercritical fluid extraction runs on Composition B are carried out at the conditions indicated in Table 2. The upper pressure of 5,500 lb/in² used in these extractions corresponds to the maximum operating pressure for standard 3/8 - 1/2 inch outer diameter stainless steel tubing that would be used in a large scale SFE processing facility. While a thicker tubing wall thickness would allow operation at higher pressures, the added cost of the tubing and associated components would drive up the cost of facility. The carbon dioxide flow rates listed in Table 2 are the actual experimental values used in each run, as measured at the syringe pump. Since the pump is heated to the temperatures listed in Table 2, these flow rates correspond to the actual flow of supercritical carbon dioxide through the extraction vessel. Extraction vessel loading of Composition B is usually limited to no more than about 20% of the vessel volume. Ideally, one desires about 6 volume exchanges of carbon dioxide throughout a 30 minute extraction. For a 7.5-ml extraction vessel, this is accomplished by using a flow rate of 1.5 ml carbon dioxide per minute. The solvent-to-feed ratio (S/F) listed in Table 2 for Composition B is the total mass of carbon dioxide used per gram of Composition B for each extraction run. The S/F values listed in Table 2 for TNT are based on a nominal 40 wt% loading of TNT in Composition B.

The morphology of Composition B can be thought of as a collection of RDX crystals that are held together by a "glue" of TNT and wax. The last column of Table 2 is a qualitative visual assessment of how well this glue is removed under the experimental conditions used. An effective extraction will remove enough of the TNT and wax to allow the Composition B sample to essentially disintegrate into a pile of separated RDX crystals. Extraction runs in

which a large fraction of the Composition B sample is still aggregated as a lump at the end of the extraction are considered to be not effective.

Table 2. Conditions and results for carbon dioxide (CO₂) SFE of Composition B.

Temp. (°C)	Press. (lb/in ²)	Mass Comp. B (gram)	Extraction Time (minute)	Average Flow Rate (ml/min.)	Mass CO ₂ (gram)	S/F (Comp. B) ^a	S/F (TNT) ^b	Result
50	2,000	0.187	30	1.2	24.5	130	326	Not effective
80	3,000	0.600	30	1.5	26.6	44	111	Not effective
85	3,000	0.786	35	1.6	31.2	40	99	Not effective
65	5,500	0.261	25	1.5	31.7	121	304	Not Effective
65	5,500	0.556	126	1.0	103.7	187	467	Effective
65	5,500	0.164	39	1.3	42.2	257	643	Effective
80	5,500	0.288	11	4.6	40.7	141	353	Not Effective
85	5,500	0.629	70	1.6	90.3	144	359	Effective
85	5,500	0.599	32	1.2	29.7	50	124	Effective

^a Solvent-to-feed ratio: grams of carbon dioxide per gram Composition B used in extraction run.

^b Solvent-to-feed ratio based on grams of TNT (40 wt%) in Composition B sample.

The solubility data for TNT in carbon dioxide can be used to determine the minimum required S/F. Under ideal conditions, which result in full saturation of the extraction solvent, S/F will be the reciprocal of the TNT solubility. Ideal saturation conditions generally require the use of low solvent flow rates, extraction from finely divided powders, and full loading of the extraction vessel. One of the objectives of this work is to minimize or eliminate the need for size reduction of the Composition B prior to extraction. It is also expected that volume loading of the extraction vessel will never exceed 20%. Given these considerations, actual required S/Fs for the SFE of Composition B are expected to far exceed the ideal S/Fs determined from the TNT solubility data.

The solubility of TNT in carbon dioxide at 50 °C and 2,000 lb/in² is expected to be less than 0.5 wt%, or 5 mg TNT per gram of carbon dioxide.[2] For the extraction of TNT using supercritical carbon dioxide at 50 °C and 2,000 lb/in², the required S/F will be greater than 200. In the case of the initial demonstration using a mixture of RDX and TNT powders, the actual S/F that is used for the extraction of TNT exceeds 1400; this figure is based on the use of 210 grams of carbon dioxide to extract 146 mg of TNT. Given the nature of this sample - a finely divided powder - it is expected that a much lower S/F would have sufficed. In the case of extraction of TNT from Composition B under these temperature and pressure conditions (see Table 2), a S/F(TNT) of 326 is not effective for the removal of TNT from Composition B.

At 3,000 lb/in² and 80 °C and 85 °C, the solubility of TNT in carbon dioxide is about 1 wt%, or 10 mg TNT per gram of carbon dioxide.[2] Under these conditions, the ideal S/F(TNT) is about 100. Extractions carried out right around this S/F value are not effective for the removal of TNT from Composition B.

TNT solubilities in neat carbon dioxide at a pressure of 5,500 lb/in² are about 3.7 wt% at 65 °C and about 4 wt% at 80 °C and 85 °C.[2] Within this range of temperatures, the ideal S/F(TNT) is in a range of 24 to 26. Extractions carried out at 65 °C and 80 °C are found to be effective only when a relatively high S/F(TNT) of at least 467 is used. The large mass of solvent required to carry out the separation under these conditions is believed to be due to extraction primarily from the surface of the Composition B sample. As TNT is removed, the porosity of the sample would increase, exposing more of the TNT internal to the surface of the sample to the carbon dioxide extraction solvent.

It is interesting to note that the S/F requirements drop dramatically when the extraction temperature is raised to 85 °C while maintaining a pressure of 5,500 lb/in². Comparable masses of carbon dioxide are used in the extraction runs at 80 °C (S/F of 353) and 85 °C (S/Fs of 359), but only the extraction carried out at the higher temperature is effective. The greater efficacy of the process carried out at 85 °C is apparent when one considers that if S/F is decreased from 359 to a third of this level (S/F = 124), the process is still effective at 85 °C. TNT is known to melt around 81 °C.[4] It is well known that it is easier to extract materials in their melt-phase relative to their solid phase.[5] Since there is no substantial difference in the solubility of TNT in carbon dioxide at a pressure of 5,500 lb/in² and temperatures of 80 °C versus 85 °C, the enhanced extraction of TNT at 85 °C is attributed to melting of the TNT.

Additional successful extractions of TNT from Composition B are also carried out at 7,500 lb/in² and 90 °C.

The resulting products of the successful separation are a powder of mostly crystalline nitramine, which is reclaimed from the extraction vessel, and a more finely-divided powder of TNT, which is recovered after nucleation in the carbon dioxide expansion at the outlet of the flow restrictor. Chromatograms of these materials, along with unextracted Composition B, are shown in Figure 2. Upon examination of these chromatograms, it is clear that the TNT is extracted from the Composition B in excess of 99%. It is interesting to note that both RDX and HMX appear to be extracted from the Composition B. A greater fraction of the HMX appears to be extracted from the Composition B relative to RDX. If this is indeed the case, it is a little surprising, since HMX is believed to be less soluble in neat carbon dioxide than is RDX.[1] One possibility offered here is that TNT may act as a cosolvent modifier, preferentially enhancing the extraction of HMX relative to RDX. It is known that HMX forms complexes with many compounds that do not form equivalent RDX complexes.[6]

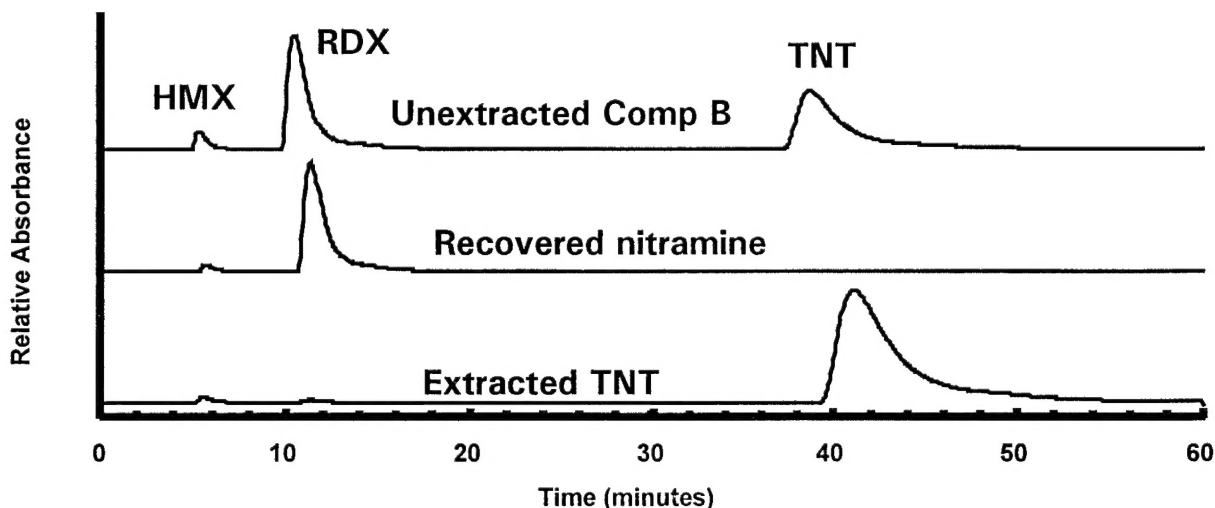


Figure 2. Chromatograms of unextracted Composition B, recovered nitramine, and extracted TNT. Extraction is carried out at 85 °C and 5,500 lb/in².

The desensitizing wax that is used in Composition B needs to be accounted for. Waxes are generally extractable using supercritical carbon dioxide. Ashraf-Khorassani and Taylor demonstrated that Candelilla wax is solubilized in carbon dioxide using conditions of 4,600 lb/in² and 60 °C.[7] Extraction of the wax from Composition B is confirmed in a qualitative manner by dissolving quantities of Composition B, the recovered nitramine, and the extracted TNT in acetonitrile. The wax is observed as an insoluble solid in the Composition B/acetonitrile solution. A substantial quantity of the wax is observed in the TNT/acetonitrile solution, while only small amounts of wax are observed in the nitramine/acetonitrile solution, indicating that the majority of the wax has been extracted from the Composition B along with the TNT.

Nitramine washing. The RDX recovered from the SFE process does not have the milky white appearance normally seen in freshly recrystallized RDX, but rather has a brownish-yellow color. Since the HPLC analysis of this material reveals the presence of no substantial quantity of impurity, it is suspected that this discoloration is due to a surface coating on the RDX crystals themselves. To investigate this possibility further, some of the recovered RDX is washed in a small quantity of acetonitrile. The quantity of solvent is kept small enough to prevent substantial dissolving of the nitramine. The solution, which rapidly takes on a yellowish-brown tint, is filtered off of the RDX. The result of solvent washing of the nitramine is a crystalline material with a much whiter appearance.

The nature of the discoloration probably stems from the way in which RDX and TNT are processed in the manufacture of Composition B. Composition B undergoes at least 2 melt-freeze cycles in the production of a filled ordnance item. TNT and RDX, along with the desensitizing wax, are initially prepared as a melt that is cast as a thin sheet. Once the sheet has solidified, it is broken into flake. The Composition B flake is eventually remelted and cast as a fill. RDX has a solubility of about 5 wt% in molten TNT, with a eutectic of 4.15% RDX at 79 °C.[8] As the Composition B solidifies following a melt operation, it is reasonable to expect the formation of an intimately-combined RDX/TNT solid at the interface between the RDX crystal and the bulk volume of TNT. It is possible that TNT - or a TNT-related impurity - trapped just below the surface of the RDX crystal may not be readily removed during the extraction operation. Since dissolution of a crystal begins with its exterior surface, the presence and removal of trapped TNT would account for the whitening of the RDX that is observed when the nitramine is washed with acetonitrile. If the discoloration of the RDX is due instead to some sort of thermal decomposition throughout the nitramine crystals, solvent washing would not give the same result as what is observed.

Extraction of TNT from Composition B using acetonitrile-modified carbon dioxide. Since acetonitrile works well as a wash solvent for the nitramine recovered from neat carbon dioxide extraction runs, it may be possible to get similar results in a single step by using acetonitrile as a modifier in the extraction of Composition B. A 4 mole% solution of acetonitrile in carbon dioxide is prepared in the cylinder of the syringe pump. Two extractions are carried out at 7,500 lb/in² and 90 °C. A second syringe pump (not shown in Figure 1) is filled with neat carbon dioxide, and is used to flush the acetonitrile from the extraction vessel at the end of the extraction run. The extracted TNT is collected in acetonitrile and the resulting solution is filtered to remove the undissolved desensitizing wax. The collection solutions are analyzed for RDX, HMX, and TNT using HPLC.

The nitramine recovered from Composition B using an acetonitrile modifier differs little in appearance from that recovered in extraction runs using neat carbon dioxide. Chromatographic analyses of the acetonitrile collection solutions reveal that 93 - 95% of the energetic material extracted - exclusive of the wax - is TNT when an acetonitrile modifier is used. Similar analyses for runs in which neat carbon dioxide is used reveal that the extracted energetic material is 96 - 98% TNT. The difference in the TNT content in the extracted material is due to the fact that RDX is much more soluble in carbon dioxide in the presence of a polar modifier like acetonitrile.[9] The use of acetonitrile as a modifier results in increased extraction of RDX, decreasing the effective separation selectivity for TNT.

One explanation for the observation that acetonitrile as a modifier is not as effective at removing the impurities on the nitramine crystals as is the neat acetonitrile wash lies in a consideration of the dielectric constant of the solvent. Neat acetonitrile at room temperature has a dielectric constant of 38. The dielectric constant for neat carbon dioxide is about 2. A solution of 4 mole% acetonitrile in carbon dioxide would have a bulk dielectric constant of about 3.5. Even though it is well known that regions of local high density exist in supercritical solutions, it is unlikely that the local dielectric constant in these regions approaches anything near that of the neat modifier solvent. An educated guess would place the upper limit of local dielectric constant of this solution at around 10.

The limited effectiveness of acetonitrile-modified carbon dioxide in carrying out TNT extraction and washing of the nitramine in a single step is not necessarily a negative result. Incorporation of an organic modifier into a large scale carbon dioxide extraction apparatus would result in an increase in capital equipment costs, require a more complex TNT separation stage, and increase the amount of waste produced by the process.

TNT Purification. Using the equipment shown in Figure 1, the TNT that was extracted from the Composition B is extracted a second time using milder temperature and pressure conditions. Three extraction runs are carried out at

2,000 lb/in² and 50 °C, 1,500 lb/in² and 20 °C, and 1,000 lb/in² and 20 °C. Under these conditions, RDX and HMX are expected to possess very limited solubilities in neat carbon dioxide. The TNT reprocessed in this manner appears much whiter than that initially extracted from the Composition B. No HMX is observed in the chromatograms run on the reprocessed TNT. Small amounts of wax are observed when these samples are dissolved in acetonitrile. Given the mild extraction conditions used, it is expected that the majority of the wax is left behind in the extraction vessel, especially in the cases where subcritical carbon dioxide is used at room temperature. Basing the compositional analysis on the presence of only RDX and TNT, all three of these extractions result in TNT purities in excess of 99.4 wt%.

The results obtained indicate that it should be possible to combine the initial extraction of the TNT from Composition B with the TNT reprocessing step by inclusion of an additional pressure and temperature fractionation stage in the extraction scheme. While a two-step fractionation apparatus has not been demonstrated as part of this work, all that would be involved is the addition of an additional pressure reduction valve and a lower pressure vessel. Assembly of such equipment is well within the current state of the art of chemical processing technology.

CONCLUSIONS

In this paper a supercritical fluid extraction process is described, which results in the separation of TNT and RDX from Composition B high explosive. The following conclusions are made regarding this process:

1. Supercritical fluid extraction employing only neat carbon dioxide as an extraction solvent results in an environmentally-friendly, potentially zero waste process.
2. The process selectively extracts TNT in the presence of RDX. The recovered nitramine is greater than 99% TNT-free. It is estimated that the extracted material is about 95% TNT, with small amounts of wax, RDX, and HMX being coextracted.
3. The recovered nitramine has a brownish-yellow color. This color is believed to be due to unextracted TNT - or TNT-related compounds - bound at the surface of the nitramine crystal. Washing of the nitramine in acetonitrile whitens the color of the nitramine by removing material at the surface of the crystal.
4. Purification of the TNT is easily accomplished by reprocessing with liquid carbon dioxide at room temperature and a pressure of about 1,500 lb/in².
5. Supercritical fluid extraction employing acetonitrile-modified carbon dioxide results in recovered nitramine with about the same appearance as that recovered from extractions in which neat carbon dioxide is employed. A higher level of RDX is coextracted with the TNT when the modifier is used versus the situation when only neat carbon dioxide is used, resulting in a decrease in separation specificity for TNT. The use of acetonitrile as a modifier for extraction of TNT from Composition B is not recommended.
6. Supercritical fluid extraction of Composition B is most effective when carried out at temperatures above the TNT melting point of 81 °C. At these temperatures, extraction pressures of 5,500 lb/in², or higher, are recommended to maintain sufficient solvent density.
7. No sample size reduction is required for the lab-scale samples used in this study.
8. The process should be easily adapted to closed-loop operation, minimizing discharge and loss of carbon dioxide to the environment.
9. It should be possible to directly apply this process to other TNT-based energetic materials, including octol (HMX/TNT) and tritonal (TNT/aluminum), or the extraction of TNT residues from scrap metal following melt-out/steam-out of TNT-based explosives from ordnance items.

ACKNOWLEDGMENTS

This work was supported by the Strategic Environmental Research and Development Program through project PP-660.

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